

THE FRENCH REPUBLIC

PATENT

No. 1.487.497

MINISTRY OF INDUSTRY

P.V. No 63.338

C03//B60j

International classification

PATENT RIGHTS
DEPARTMENT

Official stamp: LIBRARY OF THE
UNIVERSTY OF PARIS- ORSAY

Laminated security glass

Company name: MONSANTO COMPANY headquartered in the United States of America.

Applied for in Paris on 27 May , at 15h 57 mm .

Issued pursuant to Decree of 29 May 1967.

(Official patent rights bulletin No. 27 of 7 July 1967.)

(Patent the issuing of which was adjourned in accordance with Article II, Section 7 of the law dated 5 July 1844, modified by the law of 7 April 1902.)

The invention concerns improved, laminated security glass, especially laminated security glass with an intermediate layer of polyvinyl acetal, which has higher penetration resistance. Laminated security glass contains at least two glass panels bound together by an intermediate layer of adhesive transparent plastic. The normal plastic intermediate layer is plasticized polyvinyl acetal resin in form of a sheet or foil, with a thickness of about 0.38 mm or more. The main industrial use of these security glass components concerns automobile windscreens as well as windscreens for other motor vehicles. There is a growing need for improved laminated security glass due to the ever-increasing number of automobiles, the higher speed at which vehicles move, and the larger surface of modern windscreens. These windscreens not only protect the people inside a vehicle from objects (stones, etc.) projected from the exterior, they also prevent the vehicle occupants from violently bumping into the windscreens if the vehicle stops brutally. The danger of being cut by the windscreens glass can occur not only when an object hits and crosses the windscreens, but also when the windscreens breaks and glass fragments are released. The intermediate layer is advantageous not only because it holds together the glass particles, but also because it can absorb the energy resulting

from an impact, which reduces the dangers of skull fracture that may occur when a person's head hits the windscreens. Moreover, this intermediate layer increases penetration resistance. The intermediate layers of windscreens, currently available at the market, also contain about 0.3 to 0.5% humidity. It was claimed that a certain increase in penetration resistance could be obtained when the humidity content of the plastic intermediate layer is considerably higher. However, the presence of high humidity alone to sufficiently improve penetration resistance is not advantageous because the clarity of the windscreens is affected negatively by the formation of bubbles between the intermediate layer itself. Furthermore, the presence of excess humidity may cause the laminated layers to peel off. Therefore, the automobile industries and the industries for laminated items have not been able to significantly use this method to improve penetration resistance.

The main objective of the invention is to produce laminated security glass with improved penetration resistance when hit by an object, more especially a human skull.

A particular objective is to improve the physical properties of laminated security glass.

A further objective of the invention is to define the procedures and the systems to achieve the above-mentioned objectives.

These and other objectives are attained using laminated security glass formed by binding two glass panels together with the help of an intermediate layer of plasticized polyvinyl acetal resin; this layer has 0.1 to 0.8 % humidity content and a sufficient amount of formate or other saturated aliphatic monocarboxylic acid potassium salts containing 3 to 22 carbon atoms to produce an alkalinity titre of 25 to 40, or a sufficient amount of saturated aliphatic dicarboxylic acid potassium salts containing 4 to 9 carbon atoms to produce alkalinity titre of 10 to less than 60.

The alkalinity titre is the number of millilitres of hydrochloric acid 0.01 N required to neutralise 100 g of polyvinyl acetal resin. This is an arbitrary method of describing the alkalinity of resin. The alkalinity titre is generally determined before lamination, by dissolving 7 g of polyvinyl acetal resin in 250 cm³ of pre-neutralised ethanol, and titrating with hydrochloric acid 0.005 N up to the end point using as indicator bromophenol blue and determining through calculation, from the result obtained, the millilitres of hydrochloric acid 0.01 N necessary for 100 g of resin.

Up till now, the standard practice has been to stabilise the polyvinyl acetates meant to form intermediate layers, with the help of potassium hydroxide or sodium hydroxide and/or potassium acetate or sodium acetate by adding small quantities of these substances. These latter are normally added while preparing the polyvinyl acetate. Large quantities of these salts or bases tend to increase the colour of the extruded plasticized resin, which is not desirable for an intermediate layer. The presence of these alkaline substances produces the alkalinity titre of standard intermediate layers of polyvinyl acetal.

The examples, which are neither exhaustive nor restrictive, are used to

explain the purpose of the invention in more detail. All the parts and percentages are indicated in weights, except where otherwise specified.

Example 1. - a. For this example, an ordinary intermediate layer of polyvinyl acetal is used for windscreens. It is made up of polyvinyl butyral containing 18.8% vinyl alcohol, with an alkalinity titre level of 20. This titre level is due to the presence of potassium acetate in the polyvinyl butyral. The resin is plasticized, with 44 parts of di (2 - ethyl butyrate) triethylene glycol and about 0.4% humidity content. The intermediate layer is formed by a sheet which is about 0.38 mm thick. This intermediate sheet is used as reference or control.

A group of ten laminated glasses are prepared individually by inserting the intermediate layer of vinyl butyral between two 61 x 915 x 3,15 mm glass panels.

The laminated glasses thus obtained are then subjected to a temperature of about 135° under a pressure of 13 kg/cm² for about 10 minutes, to bind the panels to each other.

Other laminated glass groups are prepared in the same way using a polyvinyl butyral compound with different potassium acetate contents to produce the following alkalinity levels:

b. 29; c. 42; d. 56.

The laminated glasses prepared using the above-mentioned method are then subjected to "average height of drop for breakage" tests, in accordance with the experimental specifications of the Society of Automotive Engineers - Subcommittee on automobile windows panes or glasses - and the results are indicated in table I.

In principle, the "average height of drop for breakage" test consists in placing the laminated glass in a horizontal position by supporting it with a frame or along its edges while it is subjected to a temperature of 21°. A 10 kg ball (considered to have the shape of a head) is then dropped from a specified height, approximately in the

centre of the laminated glass. This test is repeated by increasing more and more the ball's height of drop with a view to determining in centimetres the approximate height of drop at which the tested laminated glasses resist penetration. In other words, the "average height of drop for breakage" of laminated glass is a measurement of the capacity of this laminated glass to absorb the energy produced by the impact of an object.

An ordinary test was used to determine the colour of the resin used. This colour is expressed in the "percentage of yellow". A 7.5 % polyvinyl butyral resin solution is prepared by dissolving resin in methanol. This dissolution generally takes place with plasticized resin, and for resin containing 44 parts of the plasticizer per 100 resin parts, the 7.5 % solution is obtained by dissolving 5.4 parts of the plasticized resin in 44.6 parts of methanol.

Absorption-related information is obtained using a photoelectric colorimeter from Klett Summerson. The absorption is measured at 420 m μ (blue filter) and 660 m μ (red filter); the result is converted to transmission %. The subtraction of the reading at 420 m μ gives the percentage of yellow.

Example 2. – a. Another group of 10 laminated glasses is prepared in a similar manner by inserting between the glass panels an intermediate layer comprising a 0.38 mm thick sheet of plastic polyvinyl butyral resin, with this resin plasticized like in example 1 and with a humidity content of 0.4% and alkalinity titre level of 20 produced by the presence of potassium formate instead of potassium acetate.

Other groups of 10 laminated glasses are prepared as indicated above, except that the quantity of potassium formate in the polyvinyl butyral is modified to produce the following alkalinity rates: b. 30; c. 40. After being treated, the laminated glasses are tested like in example 1, and the results are indicated in table 1.

Example 3. – Similar groups of ten laminated glasses are prepared like in example 1, except that the alkalinity titre of polyvinyl butyral is produced by potassium valerate in order to obtain the following titres: a. 30; b. 40.

The results of tests conducted with the groups of laminated glasses are as follows:

TABLE I

| Example | Humidity rate | Alkalinity titre | Colour (yellow) | Average height of drop for breakage |
|---------------------|---------------|------------------|-----------------|-------------------------------------|
| | % | | % | cm |
| Potassium acetate: | | | | |
| I. a..... | 0.40 | 20 | 10.6 | 70 |
| b..... | 0.40 | 29 | 13.1 | 73 |
| c..... | 0.43 | 42 | - | 91 |
| d..... | 0.48 | 56 | 18.4 | 176 |
| Potassium formate: | | | | |
| II. a..... | 0.40 | 20 | | 73 |
| b..... | 0.41 | 26 | | 91 |
| c..... | 0.44 | 30 | | 115 |
| d..... | 0.34 | 40 | 21.0 | 213 |
| Potassium valerate: | | | | |
| III. a..... | 0.41 | 30 | 14.0 | 94 |
| b..... | 0.43 | 40 | | 115 |

The results given in table I show that the laminated glasses with intermediate layers of polyvinyl butyral containing formate or potassium valerate with a view to producing alkalinity titres have higher penetration resistance than those containing potassium acetate. However, it must be noted that the level of colour produced by potassium formate is higher than the one produced with potassium

acetate, whereas the colour produced with potassium valerate is the same as the one obtained with acetate.

Table II shows the results obtained with other examples of laminated security glasses, like in example I, except that other potassium salts are used and that the inserted resin layer is 0.76 mm thick.

TABLE II

| Example | Potassium salt | Humidity rate | Alkalinity titre | Average height of drop for breakage |
|---------|----------------|---------------|------------------|-------------------------------------|
| | | % | | cm |
| IV..... | Propionate | 0.44 | 35 | 246 |
| V..... | Octonate | 0.43 | 30 | 335 |
| VI..... | Stearate | 0.45 | 40 | 365 |

A similar group of laminated glasses prepared with a 0.76 mm thick intermediate layer of resin, with 0.41 %

humidity and alkalinity titre rate of 35, due to the presence of potassium acetate, only

has an average height of drop for breakage of 225 cm.

Example 7 to 9. – Additional groups of laminated glasses are equally prepared like in example 1 to be able to cite other

varieties of potassium salts that can be used for the intermediate resin layer to obtain improved laminated glasses, except that 0.76 mm thick intermediate layers are used.

| Example | Potassium salt | Humidity rate | Alkalinity titre | Average height of drop for breakage |
|-----------|------------------|---------------|------------------|-------------------------------------|
| | | % | | cm |
| VII..... | Isobutyrate | 0.41 | 36 | 300 |
| VIII..... | 2-ethyl butyrate | 0.50 | 38 | 335 |
| IX..... | Lactate | 0.33 | 32 | 365 |

Table III shows the results of other examples of laminated security glasses prepared like in example 1, except that a

0.76 mm thick intermediate resin layer is used.

TABLE III

| Example | Potassium salt | Humidity rate | Alkalinity titre | Average height of drop for breakage |
|-----------|----------------|---------------|------------------|-------------------------------------|
| | | % | | cm |
| X a..... | Acetate | 0.48 | 40 | 400 |
| b..... | - | 0.43 | 50 | 470 |
| XI a..... | Formate | 0.36 | 30 | 380 |
| b..... | - | 0.45 | 40 | 518 |

Example 12. – a. Another group of ten laminated glasses is prepared like in example 1 by inserting between the glass panels a 0.38 mm thick sheet of a plasticized polyvinyl butyral resin (plasticized like in example 1), with 0.4% humidity content and an alkalinity titre of 13 produced by the presence of potassium acid succinate (KH succinate) instead of potassium acetate.

Other groups of ten laminated glasses are prepared like in example 1, except that the amount of potassium acid succinate in the polyvinyl acid is modified to produce the following alkalinity tires: b. 21; c. 42; d.45.

After processing, the laminated glasses are tested like in example 1, and the results are indicated in table IV.

Example 13. – Similar groups of ten laminated glasses are prepared like in example 1, except that the alkalinity titre of polyvinyl butyral is produced by potassium succinate (K_2 succinate) to obtain the following titres: a. 14; b. 25; c. 35; d. 45.

The results of the tests with the processed group of laminated glasses are indicated in the table below:

TABLE IV

| Example | Humidity rate % | Alkalinity titre | Average height of drop for breakage Cm |
|---------------------------------|--------------------|------------------|---|
| KH succinate: | | | |
| XII a..... | 0.40 | 13 | 79.2 |
| b..... | 0.38 | 21 | 106 |
| c..... | 0.49 | 35 | 167 |
| d..... | 0.42 | 45 | 213 |
| K₂ succinate: | | | |
| XIII a..... | 0.40 | 14 | 73 |
| b..... | 0.43 | 25 | 82 |
| c..... | 0.41 | 35 | 122 |
| d..... | 0.41 | 45 | 176 |

The results indicated in the above table show that the laminated glasses in which the inserted polyvinyl butyral layers contain potassium acid succinate or potassium succinate with a view to obtaining the alkalinity titre have higher penetration resistance than those containing potassium acetate like in example 1.

Table V shows the results of other examples of laminated security glasses prepared like in example 1, except that

other salts are used in the intermediate resin layers; these layers are 0.76 mm thick, whereas the glass panels are about 300 x 300 mm. The test used to determine the "average height of drop for breakage" in centimetres is the same as that of example 1, except that a 2.26 kg steel ball is used. The results are the same as those obtained through the tests with a 10 kg ball in example 1.

TABLE V

| Example | Salt | Humidity rate % | Alkalinity titre | Average height of drop for breakage cm |
|-----------|--------------------------|--------------------|------------------|---|
| I a..... | K acetate | 0.44 | 20 | 228 |
| b..... | K acetate | 0.42 | 30 | 325 |
| c..... | K acetate | 0.45 | 42 | 400 |
| d..... | K acetate | 0.41 | 56 | 480 |
| XIV | | | | |
| a..... | Na acetate | 0.41 | 20 | 225 |
| b..... | Na acetate | 0.40 | 40 | 312 |
| c..... | Na acetate | 0.44 | 56 | 335 |
| XV..... | KH succinate | 0.41 | 21 | 426 |
| XVI..... | K ₂ succinate | 0.42 | 35 | 457 |
| XVII..... | K ₂ glutarate | 0.40 | 25 | 396 |
| XVIII | | | | |
| a..... | KH glutarate | 0.39 | 12 | 380 |
| b..... | KH glutarate | 0.42 | 23 | 465 |
| c..... | KH glutarate | 0.41 | 33 | 560 |
| d..... | KH glutarate | 0.41 | 57 | 590 |

Examples 19 to 22. – Additional groups of laminated glass are prepared as indicated in example 1 to cite other varieties of potassium salts that can be used for the intermediate layer in order to obtain improved laminated glass, except that the layers are 0.76 mm thick. The tests are the same as for example 1.

Example 23. – The same method as in example 1 is used to produce groups of laminated glasses with a view to citing other potassium salts that do not have any advantageous impact on the penetration resistance of laminated glasses. In this case, the intermediate layers are 0.38 mm thick.

(See table on the next page)

The titres indicated there as "acids" a, d, f, and h are obtained with potassium salts that do not produce any alkaline reaction with bromophenol blue. The quantity of salt used is equal to the one indicated in the

preceding line. The aromatic polyacids used in e, f, g, and h are not compatible with resin in that they produce foggy laminated glasses.

Unexpectedly, the intermediate layers established according to the invention have low adhesion to glass. For the titres produced by potassium acetate, it has been noticed that titres below 25 are necessary to obtain good adhesion. The adhesion rate can be measured in several ways, for instance through a grab strength test.

This test consists in laminating, with the effect of heat and pressure, an intermediate layer of 215 x 82 mm plasticized polyvinyl butyral between a 150 x 75 mm glass panel and a 0.15 mm thick aluminium sheet measuring 230 x 82 mm. The intermediate layer in the laminated glass is obtained with a thickness of 0.25 mm. The side of the aluminium sheet in contact with the intermediate layer is covered with phenol polyvinyl butyral in order to obtain higher

adhesion between the intermediate layer and aluminium.

| Example | | Humidity | Alkalinity titre | Average height of drop for breakage |
|---------|--|----------|------------------|-------------------------------------|
| | | % | | cm |
| XXIII | | | | |
| a..... | K ₂ oxalate | 0.34 | 28 | 60 |
| b..... | KH oxalate | 0.33 | Acid | 70 |
| c..... | K ₂ malonate | 0.36 | 28 | 70 |
| d..... | KH malonate | 0.53 | Acid | 70 |
| e..... | K ₁ benzophenol tetracarboxylate | 0.48 | 20 | 70 |
| f..... | K ₂ H ₂ benzophenol tetracarboxylate | 0.40 | Acid | 73 |
| g..... | K ₃ trimelitate | 0.43 | 10 | 70 |
| h..... | K _{1.5} H _{1.5} trimelitate | 0.42 | Acid | 106 |
| i..... | K ₂ CO ₃ | 0.63 | 29 | 70 |
| j..... | KHCO | 0.58 | 27 | 70 |
| k..... | K ₃ PO ₄ | 0.45 | 26 | 64 |
| l..... | KH ₂ PO ₄ | 0.38 | 40 | 64 |
| m..... | K ₂ HPO ₄ | 0.39 | 40 | 60 |

The laminated edges are cut according to the glass dimensions before lamination. The laminated glasses are then subjected to a test in an Instron tensile test machine, by pulling on the aluminium sheet which is detached to part the glass at an angle of 90°, with the sheet moving with the

intermediate layer that adheres to it at a speed of about 125 mm per minute. The pick strength is determined as the average force in kilo necessary to separate the glass resin by 2.5 cm from the specimen. The results are indicated as the average for at least two similar specimens tested.

TABLE VI

| Example | Salt | Humidity % | Alkalinity titre | Average height of drop for breakage kg |
|---------|------------------------|---------------|------------------|---|
| XXIV | | | | |
| a..... | K acetate | 0.41 | 10 | 10.5 |
| b..... | K acetate | 0.43 | 15 | 9.7 |
| c..... | K acetate | 0.44 | 20 | 9.5 |
| | | | 25 | 8.4 |
| XXV | | | | |
| a..... | KH succinate | 0.40 | 13 | 7.2 |
| b..... | KH succinate | 0.41 | 21 | 5.4 |
| XXVI | | | | |
| a..... | KH glutarate | 0.59 | 12 | 6.3 |
| b..... | KH glutarate | 0.40 | 23 | 4.5 |
| c..... | K ₂ adipate | 0.41 | 25 | 7.2 |

The potassium salts incorporated into the intermediate layers of polyvinyl acetal, which are the subject-matter of the invention and are saturated dicarboxylic acids with 4 to 9 carbon atoms comprise acid salts such as succinic acid, glutaric acid, adipic acid, pimelic acid and azelaic acids, as well as substitute products of these acids like 1,2 - methylsuccinic acid, tartaric (dihydroxy-succinic) acid and similar acids, as well as mixtures of any of

the above-mentioned acids. Substituted acids may contain those with hydroxy, chloro, phenyl or amino substituants. These salts comprise complete salts as well as acid salts of any or all of the above-mentioned acids. Dibasic acids containing 4 to 6 carbon atoms, as well as the substitute derivatives of these acids, are specially preferred.

The potassium acids incorporated into the intermediate layers, the subject-matter of this invention, and which are saturated aliphatic monocarboxylic acid salts containing 3 to 22 carbon atoms, comprise propionic, butyric, valeric, hexanoic, octanoic, decanoic, lauric (dodecanoic), stearic, docosanoic and similar acid salts and compounds of these acids. They equally contain acids such as isobutyric acid, 2-ethylbutyric acid, 2-ethylhexanoic acid, isodecanoic acid and similar acids. They also contain substituted acids like their hydroxyl, aryl or halogenated derivatives. The substituted hydroxyl acids may contain hydroxybutyric acid, hydroxyvaleric acids, hydroxycaproic (leucinic) acid and the like. The use of compounds of the above-mentioned acids is equally envisaged. It is well known that increasing the thickness of the intermediate layer of plasticized polyvinyl butyral improves to a certain level the penetration resistance of laminated glasses. The invention is also applicable to thicker laminated glasses. In fact, the use of a 0.76 mm thick intermediate layer containing the above-mentioned potassium carboxylates provides an "average height of drop for breakage" twice higher than the 0.38 mm indicated in the examples. One of the main objectives pursued by the security committees for higher-security automobiles is to prevent the windshield from being broken by any part of the human body in case of collision at the currently used speeds. The invention makes it possible to manufacture laminated glass-based windshields which, as shown by the test results, are not penetrated in case of collision with fixed objects, even when the automobile is moving at a speed above 40 km per hour. In other words, for normal humidity contents of the intermediate layer, if the alkalinity titre is set as indicated for the implementation of the invention, laminated glass with clearly higher security is obtained.

The laminated security glass concerned by the invention is particularly effective in that the improved penetration resistance remains over a long temperature range. The impact tests described in the examples took place at room temperature, but tests conducted at a temperature as low as -15° and as high as 49° show that these laminated glasses have improved properties within a long temperature range.

As mentioned above, the humidity content of the intermediate layer of polyvinyl butyral cannot be increased very much if the problem of bubble formation is to be avoided. Moreover, the humidity content of the intermediate layer is rather difficult to fix because it is affected by atmospheric conditions and by the special lamination process. As a result, it is preferable to keep the humidity content low. On the other hand, the alkalinity titre of the intermediate layer can easily be increased by adding the potassium salts in question while preparing polyvinyl butyral resin. It has been discovered that the minimum amount of potassium salts necessary to produce the special improvement of the penetration resistance of the final laminated glass is, to a certain level, inversely proportional to the preferred humidity rate. The preferred humidity rate is between 0.1 and 0.8% for the intermediate layers established according to the invention and having an alkalinity titre above 25. This inverse proportion is not critical between 0.3 and 0.5% humidity limits. For alkalinity titre values of 25 or less, you may be obliged to increase the humidity content up to an undesirable value for most ordinary lamination operations, which tends towards the formation of bubbles or blisters in the final laminated glass.

Table VII shows the lack of impact or the impact of humidity, in the normal humidity range, in the absence of any salts, on the shock resistance of various groups of laminated glasses. The plasticized

intermediate layers with zero alkaline titre were prepared from resin that had been carefully washed after it had swollen in a mixture of alcohol and water, as described below.

| Alkalinity titre | Humidity | Average height of drop for breakage | |
|---------------------|----------|--|------------------|
| | | 0.38 mm | 0.76 mm layer |

| | | layer | |
|--------|------|-------|-----|
| | % | cm | cm |
| 0..... | 0.06 | 70 | 228 |
| 0..... | 0.31 | 70 | 228 |
| 0..... | 0.37 | 70 | 228 |
| 0..... | 0.50 | 70 | 228 |
| 0..... | 0.75 | 70 | 228 |

To prevent corrosion by the alkali while producing resin with the help of formate and monocarboxylic acid salts, and to prevent the intermediate layers from being excessively sensitive to humidity, which

can occur on the joints formed at the edges between intermediate layer laminations, it is highly preferable to limit the alkalinity value to maximum 40.

For the reason given above, when dicarboxylic salts are used for a preferred mode of the invention, the alkalinity titre is limited to less than 60 for a humidity rate between 0.1 and 0.8 %. The lower efficiency limit of the alkalinity titre for improved shock resistance is about 10. For a preferred humidity rate between 0.2 and 0.6 %, a preferred alkalinity titre value is between 15 and 40. In this preferred range particularly good water resistance level is attained between 15 and 25, whereas particularly high shock resistance is obtained as from 25 to 40.

For the production of laminated security glasses as described in the preceding examples, the glass and the intermediate layers of polyvinyl butyral are kept as clean as possible in carefully controlled conditions. The presence of shreds, dust, atmospheric oil, etc., on the glass or intermediate layer surface affects the results in terms of the height of drop for breakage. If the glass or plastic material is highly contaminated by these impurities, the impact on the said height of drop may be big. Nevertheless, the wish of security glass manufacturers is to provide laminated glasses that are as free as possible from any contamination, which reduces this problem to a minimum.

Generally, laminated glasses are produced by inserting the plasticized intermediate layer of polyvinyl butyral between two glass panels, and subjecting the resulting set to a temperature level between 88° and 163° and a to a pressure level between 10.5 and 15.8 kg/cm² for at least 10 minutes, to bind the parts with one another.

The plastic material used as intermediate layer within the framework of the invention is plasticized polyvinyl butyral. Other polyvinyl acetals, such as acetaldehyde or propionaldehyde acetals or a mixture of both may also be used. In general, the thickness of the intermediate

layer used to laminate the security glass is above 0.25 mm. The laminated glass normally used for automobile windshields is generally about 0.38 mm thick. However, laminated glasses have been produced for various applications in which the thickness of the intermediate layer varies between 0.25 and 1.65 mm. A laminated glass particularly advantageous for its use on windshields that cannot be penetrated by a human head in case of shock due to a collision between a vehicle and fixed objects at speeds above 32 km/h is the one whose intermediate layer has an alkalinity titre value above 30 and is between 0.65 and 0.99 mm thick, with a humidity level within the normal limits, i.e. between 0.1 and 0.8%.

The preparation of polyvinyl acetal resin is well known. Generally, resin is prepared by first hydrolysing polyvinyl acetate. The hydrolysed product is then made to react with butyraldehyde in an ethanolic solution, with an appropriate quantity of sulphuric acid. The reactions are handled in such a way that polyvinyl butyral resin is obtained, with approximately 9 to 30 % hydroxyl that did not react, calculated in % weight of vinyl alcohol, and about 0.3 % ester calculated in % weight of vinyl acetate, the balancing product being vinyl butyral. The product obtained may be precipitated in ethanol through the addition of water, followed by repeated washing in water until the entire acid is removed. After the acid has been removed, the product is stabilised by being treated with potassium hydroxide or sodium hydroxide while this product is suspended in an aqueous ethanol solution containing about 30 % ethanol. About 100 parts of resin are used for 1000 parts from the suspension area. The suspension is maintained at 40° for several hours, shaken moderately and maintained in a slightly alkaline condition for phenolphthalein through the addition of appropriate quantities of potassium hydroxide or sodium hydroxide. The

polyvinyl acetal resin is then separated from the suspension area and washed with water.

At this stage, the water contains approximately 20 to 30 ml of alkalinity titre, basically comprising potassium acetate or sodium acetate. To replace these salts with the ones used in accordance with the invention, the resin is allowed to swell in a mixture of alcohol and water (density: 0.960) at 40° for one hour and is carefully washed with water until the dried resin becomes neutral for bromophenol blue, for alkalinity titre test. Appropriate quantities of salts, established according to the invention, are then added to a suspension of washed resin with zero alkalinity titre (5 parts of water for each resin part). After 30

minutes, the grains are filtered and dried. A more even distribution of the salts is produced by the plastification operation.

To add the salts to the resin with zero alkalinity titre, a variant consists in incorporating these salts with the plasticizer during the plastification operation.

Obviously, and as it also already results from the aforementioned, the invention does not just limit itself to that of its application modes, nor to those of the application modes of its various parts that have been specially mentioned. On the contrary, it covers all the variants.

SUMMARY

The invention concerns an improved laminated security glass comprising two glass layers bound to an intermediate layer of plasticized polyvinyl acetal; the intermediate layer contains 0.01 to 0.8% humidity and at least one element chosen in the group consisting of potassium formate, saturated aliphatic monocarboxylic acid potassium salts with 3 to 22 carbon atoms and saturated aliphatic dicarboxylic acid potassium salts with 4 to 9 carbon atoms, in sufficient quantity to produce an alkalinity titre value between 25 and 40, in case of formate and monocarboxylic acid salts, and between 10 and less than 60, in case of dicarboxylic acid salts.

Moreover, the afore-mentioned security glass can have the following characteristics, considered separately or together:

1. The polyvinyl acetal is polyvinyl butyral.
2. The intermediate layer is between 0.25 and 1.65 mm thick.
3. The intermediate layer is between 0.63 and 0.89 mm thick, and the alkalinity titre is above 25 or 30.
4. The vinyl alcohol content of the polyvinyl butyral is between 9 and 30% in terms of weight.
5. The polyvinyl butyral is plasticized with 20 to 50 parts of a plasticizer for 100 parts of butyral.
6. The alkalinity titre value is between 15 and 40, more especially between 25 and 40.
7. The dicarboxylic acid is succinic, glutaric or adipic acid;

8. The invention also concerns an improved intermediate layer for laminated security glass, characterised by the fact that it consists of plasticized polyvinyl acetal, such as polyvinyl butyral containing between 0.01 and 0.8% humidity and at least one element chosen in the group consisting of potassium formate, saturated aliphatic monocarboxylic acid potassium salts with 3 to 22 carbon atoms and saturated aliphatic dicarboxylic acid potassium salts with 4 to 9 carbon atoms, in sufficient quantity to produce an alkalinity titre value between 25 and 40, in case of formate and monocarboxylic acid salts, and between 10 and less than 60, in case of dicarboxylic acid salts.
9. The invention also concerns a procedure for producing an improved laminated security glass. The said procedure consists in inserting an intermediate layer of plasticized polyvinyl acetal between two glass panels; the intermediate layer contains 0.01 to 0.8% humidity and a sufficient quantity of potassium formate or of saturated aliphatic monocarboxylic acid potassium salts with 3 to 22 carbon atoms to produce an alkalinity titre value between 25 and 40, or of saturated aliphatic dicarboxylic acid potassium salts with 4 to 9 carbon atoms to produce an alkalinity titre value between 10 and less than 60. The lot is then subjected to pressure ranging from 10.5 to 15.8 kg/cm² and to a temperature between 88° and 163° for at least 10 minutes in order to bind the intermediate layer to the glass panels.

10. Furthermore, the invention concerns the procedure for producing an intermediate layer of improved plastic polyvinyl acetal, consisting in allowing polyvinyl acetal resin to swell in a mixture of alcohol and water at 40° for about one hour, and washing the resin carefully with water until it has zero alkalinity titre, then adding to the aqueous suspension a sufficient amount of potassium formate or of saturated aliphatic monocarboxylic acid potassium salts with 3 to 22

carbon atoms to produce an alkalinity titre value between 25 and 40, or of saturated aliphatic dicarboxylic acid potassium salts with 4 to 9 carbon atoms to produce an alkalinity titre value between 10 and less than 60, then setting the humidity content of the polyvinyl acetal to between 0.1 to 0.8 %, and then plasticizing the polyvinyl acetal and forming the intermediate layer.

Company name: MONSANTO COMPANY

By proxy:

PLASSERAUD, DEVAN, GUTMANN, JAQUELIN, LEMOINE

For the sale of the booklets, please contact IMPRIMERIE NATIONALE, 27, rue de la Convention, Paris (15th).